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IR Photodissociation Spectroscopy for Cluster Ions of Triatomic Molecules

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【Introduction】

Ion-molecule complexes play significant roles as chemical intermediates in a number of chemical reactions. For example, the formation of the chemical bond between unsaturated groups such as C=C and C=O and ions is thought to be primary processes in nucleophilic additional reactions catalyzed by acid and base. In this study, we apply IR photodissociation (IRPD) spectroscopy in the 1000–2300 cm^{-1} region to the $(CO_2)_n^+$, $(OCS)_n^+$, and $(CS_2)_n^+$ (n = 2–8) ions. In these cluster ions, an intermolecular "semi"-covalent bond will be formed between a molecular radical cation ($M^{\bullet+}$) and a neutral molecule (M) via the interference between the singly occupied molecular orbital (SOMO) of $M^{\bullet+}$ and the highest occupied MO (HOMO) of M. We discuss the characteristics of the electronic and the geometric structure of the semi-covalent bond formed in the cluster ions on the basis of the IRPD results with the aid of quantum chemical calculations.

【Experimental】

Figure 1 shows a schematic drawing of the IRPD spectrometer used in this study.[1,2] A mixture of the sample gas (CO_2, OCS, or CS_2) and Ar is injected into a source chamber through a pulsed nozzle and ionized with an electron impact ion source. The cluster ions produced are accelerated into a flight tube, and only target parent ions are mass-selected by a mass gate. Parent ions are irradiated by an output of a pulsed IR laser. Resultant fragment ions are mass-analyzed by a reflectron and detected by a multichannel plate. IRPD spectra of parent ions are obtained by plotting normalized yields of fragment ions against wavenumber of the IR laser. We also carry out the geometry optimization and the vibrational analysis of the $(CO_2)_2^+$, $(OCS)_2^+$, and $(CS_2)_2^+$ ions with GAUSSIAN03 program package at the B3LYP/6-311+G* level of theory.

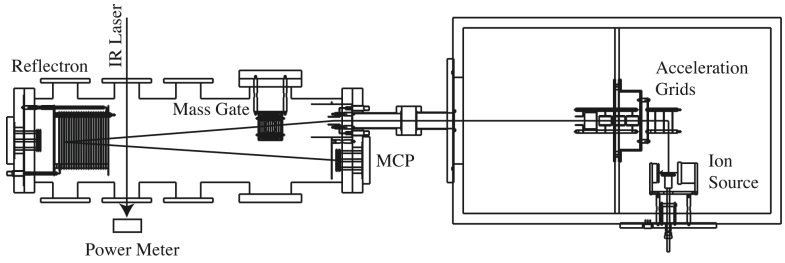

FIG. 1. Schematic drawing of the mass spectrometer for IRPD spectroscopy.

【Results and discussion】

The $(CO_2)_2^+$, $(OCS)_2^+$, and $(CS_2)_2^+$ ions are expected to have in-phase and out-of-phase combination modes of the ν_1 and ν_3 stretching vibrations of the two components. Figure 2 displays the in-phase (a) and out-of-phase (b) combination modes of the ν_3 vibrations for the $(CO_2)_2^+$ ion. If the $(CO_2)_2^+$ ion has a planar C_{2h} structure, the in-phase combination of ν_3 is IR forbidden, though the ν_3 vibration of CO_2 is strongly IR active. Therefore, the number of the IR bands of the dimer ions suggests the structural planarity. Figures 3(a), 3(c), and 3(e) show the IR spectra of the dimer ions in the ν_3 regions. In the case of $(CO_2)_2^+$ and $(CS_2)_2^+$ ions, only one band appears in the spectra, suggesting

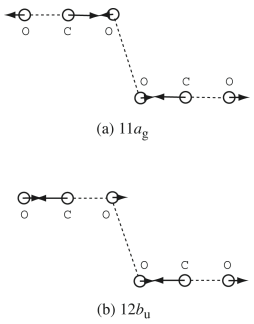

FIG. 2. Representatives of normal modes of $(CO_2)_2^+$ (C_{2h}).

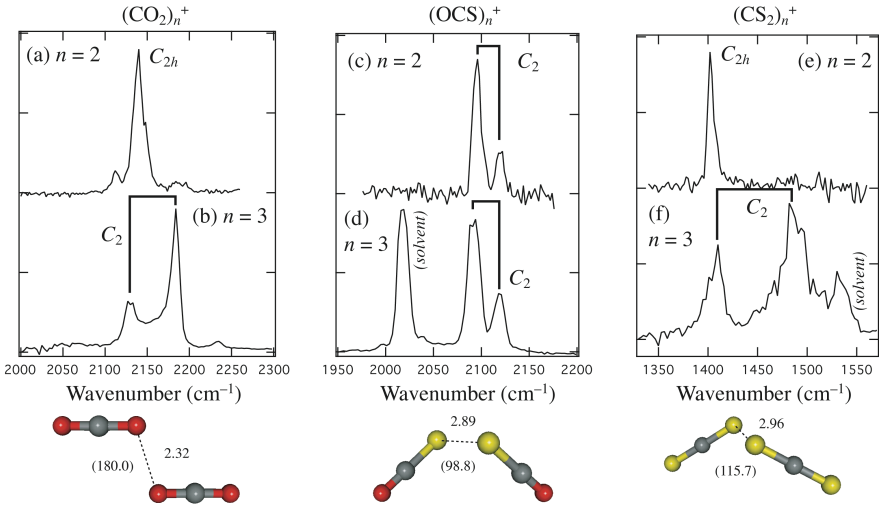

FIG. 3. IRPD spectra of the dimer and trimer ions with the optimized structures of the dimer ions for CO_2, OCS, and CS_2.

that these dimer ions have a planar C_{2h} structure. In contrast, the $(OCS)_2^+$ ion has two IR bands, which implies a C_2 structure for $(OCS)_2^+$. The IRPD results of $(CO_2)_2^+$ and $(OCS)_2^+$ are consistent with the results of the geometry optimization shown in Fig. 3; these dimer ions have a C_{2h} and a C_2 structure, respectively. However, the density functional theory (DFT) calculation provides a C_2 structure for the $(CS_2)_2^+$ ion, which does not agree with the IRPD result in Fig. 3(e). The disagreement in the $(CS_2)_2^+$ case demonstrates incomplete representation of the intermolecular interaction by the DFT calculations. In order to examine the stability of the planar form of the dimer ions, we calculate the potential energy surface (PES) of the dimer ions along the intermolecular out-of-plane bending mode (Fig. 4). The steepness of the PES is substantially lower for the $(CS_2)_2^+$ ion than for the $(CO_2)_2^+$ and $(OCS)_2^+$ ions, suggesting that the $(CS_2)_2^+$ ion has a floppier structure than that of $(CO_2)_2^+$ and $(OCS)_2^+$. The $(OCS)_2^+$ and the $(CS_2)_2^+$ ions have a double-minimum potential, and the potential barrier between the minima is substantially higher for the $(OCS)_2^+$ ion (391 cm^{-1}) than for the $(CS_2)_2^+$ ion (92 cm^{-1}). The DFT calculation predicts that the zero-vibrational level along the dihedral angle is located lower than the potential barrier even in the case of the $(CS_2)_2^+$ ion. It is probable that the DFT calculations cannot reproduce the intermolecular PES properly for the $(CS_2)_2^+$ ion because of a much weaker intermolecular interaction in $(CS_2)_2^+$. In Figs. 3(b), 3(d), and 3(f), the IRPD spectra of the trimer ions are shown for comparison. As seen in Fig. 3(b), the $(CO_2)_2^+$ ion core in the $(CO_2)_3^+$ trimer ion has a C_2 structure; the solvation of one CO_2 molecule to the $(CO_2)_2^+$ ion core easily distorts the planar structure of the dimer ion, even though the $(CO_2)_2^+$ ion has the highest tension of the planar form among $(CO_2)_2^+$, $(OCS)_2^+$, and $(CS_2)_2^+$.

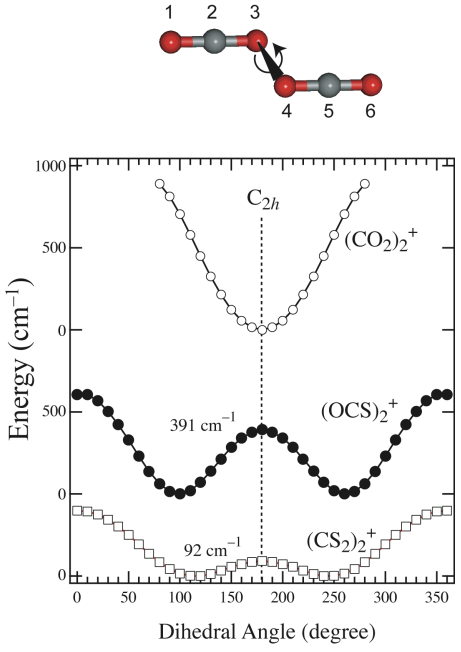

FIG. 4. Potential energy surface of the dimer ions as a function of the intermolecular dihedral angle (atoms 2–3–4–5).

【References】

(1) Y. Kobayashi, Y. Inokuchi, and T. Ebata, J. Chem. Phys. **128**, 164319 (2008).

(2) Y. Inokuchi, A. Muraoka, T. Nagata, and T. Ebata, J. Chem. Phys. **129**, 044308 (2008).